10/506547

Rec'd PCT/PTO 03 SEP 2004

DESCRIPTION

ULTRAFINE PARTICULATE TITANIUM OXIDE WITH LOW CHLORINE AND LOW RUTILE CONTENT, AND PRODUCTION PROCESS THEREOF

Cross Reference to Related Application

This application is an application filed under 35 U.S.C. §111(a) claiming benefit pursuant to 35 U.S.C. §119(e)(1) of the filing date of the Provisional Application No. 60/363,305 filed on March 11, 2002, pursuant to 35 U.S.C. §111(b).

FIELD OF THE INVENTION

The present invention relates to ultrafine particulate titanium oxide of low chlorine content and low rutile content (hereinafter may be referred to as "low-chlorine, low-rutile ultrafine particulate titanium oxide") which is suitable as an additive for silicone rubber and is suitable for use in, for example, photocatalysts, solar cells, and dielectric materials; and to a process for producing the titanium oxide. More particularly, the present invention relates to low-halogen, low-rutile ultrafine particulate titanium oxide which is obtained through vapor-phase oxidation of a titanium halogenide-containing gas by an oxidative gas at high temperature, which has a low halogen content, which enables residual halogen to be readily removed therefrom, and which exhibits excellent dispersibility; and to a process for producing the titanium oxide.

BACKGROUND

Ultrafine particulate titanium oxide has been widely employed as, for example, an ultraviolet shielding material, an additive for silicone rubber, a dielectric raw material, and a component of a cosmetic composition (as used herein, the expression "titanium oxide," which is commonly used to represent oxides of titanium, encompasses "titanium dioxide" as specified in Japanese

Industrial Standards (JIS)). Titanium oxide is also
employed in, for example, photocatalysts and solar cells.

Titanium oxide assumes any of the following three
crystal forms: rutile, anatase, and brookite. Anatase-
or brookite-type titanium oxide, which exhibits excellent
photoelectrochemical activity, is employed in
photocatalysts and solar cells, rather than rutile-type
titanium oxide.

By virtue of its photocatalytic activity, titanium
oxide is employed in, for example, antibacterial tile,
self-cleaning structural materials, and deodorant fibers
for decomposition of organic substances. The mechanism
by which titanium oxide decomposes organic substances is
as follows. Titanium oxide absorbs ultraviolet rays, to
thereby generate electrons and holes therein. The thus-
generated holes react with water adsorbed onto titanium
oxide, to thereby form hydroxy radicals. The thus-formed
radicals decompose, into carbon dioxide gas and water,
organic substances that have adsorbed onto the surfaces
of titanium oxide particles ("*Hikari Kuriin Kakumei*"
authored by Akira Fujishima, Kazuhito Hashimoto, and
Toshiya Watanabe, CMC Publishing Co., Ltd., pp 143-145,
(1997)). In titanium oxide exhibiting high
photocatalytic activity, holes are readily generated, and
the thus-generated holes readily reach the surface of the
titanium oxide. According to "*Sanka Chitan Hikari
Shokubai no Subete*" (edited by Kazuhito Hashimoto and
Akira Fujishima, CMC Publishing Co., Ltd., pp 29-30,
(1998)), anatase-type titanium oxide, titanium oxide
having small amounts of lattice defects, or titanium
oxide having small particle size and large specific
surface area exhibits high photocatalytic activity.

Studies on application of titanium oxide to solar
cells have been performed since 1991, when Graezel, *et
al.* of Ecole Polytechnique Federale de Lausanne reported
a dye-sensitized solar cell which employs titanium oxide
in combination with a ruthenium-based dye (M. Graezel,

Nature, 353, 737, (1991)). In the aforementioned dye-
sensitized solar cell, titanium oxide serves as a dye
carrier and as an n-type semiconductor, and is employed
in a dye electrode bound to an electrically conductive
glass electrode. The dye-sensitized solar cell has a
structure such that an electrolyte layer is sandwiched
between the dye electrode and a counter electrode. In
the solar cell, electrons and holes are generated through
absorption of light by the dye. The thus-generated
electrons reach the electrically conductive glass
electrode via a titanium oxide layer, and are discharged
to the outside of the glass electrode. Meanwhile, the
above-generated holes are conveyed to the counter
electrode via the electrolyte layer, and are bound to the
electrons supplied through the electrically conductive
glass electrode. In order to improve properties of such
a dye-sensitized solar cell, titanium oxide must be
readily bound to a dye. Japanese Patent Application
Laid-Open (kokai) No. 10-255863 describes that anatase-
type titanium oxide is readily bound to a dye, and
Japanese Patent Application Laid-Open (kokai) No. 2000-
340269 describes that brookite-type titanium oxide is
suitable for use in a dye-sensitized solar cell.

Functions of titanium oxide are more fully benefited
from titanium oxide of high dispersibility. Titanium
oxide of low dispersibility exhibits high hiding power.
Therefore, when titanium oxide of low dispersibility is
employed in a photocatalyst, a limitation is imposed on
use of the photocatalyst. When titanium oxide of low
dispersibility is employed in the field of solar cells,
since such titanium oxide tends not to transmit light,
the amount of light absorbed in the titanium oxide is
lowered, whereby photoelectric conversion efficiency is
lowered. In general, titanium oxide having a particle
size of about 1/2 the wavelength of visible light
exhibits maximum light scattering amount (hiding power),
and the light scattering amount is lowered in accordance

with a decrease in particle size ("Titanium Oxide"
authored by Manabu Seino, Gihodo Co., Ltd., p. 129,
(1991)). In many cases, titanium oxide having a primary
particle size of some nm to some tens of nm is employed
in the aforementioned technical field, and therefore,
titanium oxide with excellent dispersibility scatters low
amounts of light. However, titanium oxide exhibiting low
dispersibility and having large size of aggregated
particles exhibits increased light scattering.

    Therefore, titanium oxide employed in the
aforementioned technical field must exhibit high
dispersibility, and thus ultrafine particulate titanium
oxide of anatase- or brookite type, which exhibits high
dispersibility, is employed in the art. Although not
clearly defined, the primary particle size of ultrafine
particles is generally about 0.1 μm or less.

    In the case where titanium oxide is employed in a
photocatalyst or a solar cell, when a corrosive component
such as chlorine is present in the titanium oxide, a
substrate is corroded or denatured. Therefore, the
chlorine content of titanium oxide must be lowered.
Desirably, the amount of Fe, Al, Si, or S in titanium
oxide is reduced. For example, when the Fe content of
titanium oxide is excessively high, the titanium oxide is
colored, and the thus-colored titanium oxide is not
suitable for use in a material requiring transparency.
Meanwhile, when the amount of component of titanium oxide
particles, such as Al or S, is excessively large, lattice
defects are generated in the particles. When such
titanium oxide particles are employed in a photocatalyst
or a solar cell, functions thereof may be impaired.

    Production processes for titanium oxide are roughly
classified into two types: a liquid-phase process in
which titanium tetrachloride or titanyl sulfate is
hydrolyzed; and a vapor-phase process in which titanium
tetrachloride is reacted with an oxidative gas such as
oxygen or steam. Titanium oxide produced through the

liquid-phase process contains anatase as a primary phase,
but assumes the form of sol or slurry. A limitation is
imposed on the use of titanium oxide in the form of sol
or slurry. When such titanium oxide is to be employed in
5   the form of powder, the titanium oxide must be dried and
aggregation increases along with progress of drying a
titanium oxide powder which has been wetted with a
solvent ["Ultrafine Particle Handbook" edited by Shinroku
Saito, Fujitec Corporation, p 388, (1990)]. When the
10   titanium oxide powder is employed in, for example, a
photocatalyst, the titanium oxide powder must be
considerably crushed or pulverized in order to enhance
its dispersibility. Such a pulverization treatment may
cause contamination of the titanium oxide powder with
15   wear products, along with variation in the particle size
of the powder.
       In general, titanium oxide produced through the
vapor-phase process exhibits excellent dispersibility as
compared with titanium oxide produced through the liquid-
20   phase process, since a solvent is not employed in the
vapor-phase process.
       Various vapor-phase processes for producing titanium
oxide ultrafine particles have been proposed. For
example, Japanese Patent Application Laid-Open (kokai)
25   No. 6-340423 discloses a process for producing titanium
oxide through hydrolysis of titanium tetrachloride in
flame, in which proportions by mol of oxygen, titanium
tetrachloride, and hydrogen are regulated, and reaction
of these materials is allowed to proceed, to thereby
30   produce titanium oxide of high rutile content. Japanese
Patent Application Laid-Open (kokai) No. 7-316536
discloses a process for producing a crystalline
transparent titanium oxide powder having an average
primary particle size of 40 nm to 150 nm, in which
35   titanium tetrachloride is hydrolyzed at high temperature
in a vapor phase, followed by rapid cooling of the
resultant reaction product, wherein the flame temperature

and the concentration of titanium in a raw material gas
are specified. However, fine particulate titanium oxide
produced through any of the above processes has high
rutile content, and thus is not suitable for use in a
5 photocatalyst or a solar cell.

Japanese Patent Application Laid-Open (*kokai*) No. 3-
252315 discloses a vapor-phase process for producing
titanium oxide containing anatase as a primary phase, in
which the ratio of hydrogen in a gas mixture of oxygen
10 and hydrogen is varied during the course of vapor-phase
reaction, to thereby regulate the rutile content of the
resultant titanium oxide. According to this publication,
titanium oxide produced through the above process has a
rutile content of 9%. However, titanium oxide disclosed
15 in this publication has a particle size of 0.5 to 0.6 μm,
which is larger than that of a typical ultrafine
particle.

Ultrafine particulate titanium oxide is readily
produced through a vapor-phase process employing titanium
20 halogenide as a raw material, but halogen derived from
the raw material remains in the resultant titanium oxide.
Therefore, in many cases, the titanium oxide must be
subjected to dehalogenation by means of heating, washing
with water, or a similar technique. However, when the
25 ultrafine particulate titanium oxide is heated in order
to lower the chlorine content, sintering of titanium
oxide particles proceeds, whereby the specific surface
area of the titanium oxide tends to be reduced. In
addition, such heating treatment may transform the
30 crystal form of the titanium oxide from anatase to
rutile. In order to prevent reduction of the specific
surface area and such anatase-to-rutile transformation,
the titanium oxide must be subjected to low-temperature
heating or short-term heating. However, in such a case,
35 sufficient dehalogenation of the titanium oxide fails to
be attained. Japanese Patent Application Laid-Open
(*kokai*) No. 10-251021 discloses a process for lowering

the chlorine content of ultrafine particulate titanium
oxide. In this process, titanium oxide is brought into
contact with steam while the titanium oxide is rotated in
a cylindrical rotatable heating furnace, to thereby lower
5   the chlorine content. The titanium oxide described in
this publication has a rutile content as high as 15%.

When titanium oxide particles are subjected to
dehalogenation by means of, for example, washing with
water, halogen remaining on the surfaces of the particles
10   can be removed. However, halogen present in the interior
of the particles tends not to be removed, since
difficulty is encountered in bringing the halogen into
contact with water.

As described above, low-chlorine, low-rutile
15   ultrafine particulate titanium oxide cannot be produced
through conventional vapor-phase processes.

In view of the foregoing, an object of the present
invention is to provide low-halogen, low-rutile ultrafine
particulate titanium oxide which is produced through a
20   vapor-phase process and which exhibits excellent
dispersibility. Another object of the present invention
is to provide a process for producing the titanium oxide.

SUMMARY OF THE INVENTION

In order to attain the above objects, the present
25   inventors have performed extensive studies, and have
found that low-halogen, low-rutile ultrafine particulate
titanium oxide exhibiting excellent dispersibility can be
produced through a vapor-phase process. The present
invention has been accomplished on the basis of this
30   finding.

The present invention provides ultrafine particulate
titanium oxide having a rutile content as low as 5% or
less and a large BET specific surface area and exhibiting
specific properties, which is produced through a vapor-
35   phase process in which a titanium halogenide-containing
gas is reacted with an oxidative gas (for example,
oxygen, steam, or a gas mixture containing oxygen and

steam) while the heating temperature and the heating time are controlled, followed by dehalogenation. The present invention also provides a process for producing the titanium oxide.

Accordingly, the present invention provides the following.

(1) A titanium oxide produced through reaction between a titanium halide-containing gas and an oxidative gas, characterized in that the rutile content of the titanium oxide is 5% or less, and that the specific surface area of the titanium oxide as measured by means of a BET one-point method; i.e., B (m^2/g), and the chlorine content of the titanium oxide; i.e., C (mass ppm), satisfy the following relation: $C \leq 650e^{0.02B}$, and in that, when an aqueous suspension containing the titanium oxide in an amount of 1 mass% is allowed to stand at 20°C for 30 minutes, the amount of halogen which is transferred from the titanium oxide to a liquid phase is at least 80 mass% on the basis of the entire amount of halogen contained in the titanium oxide.

(2) A titanium oxide according to (1) above, wherein the amount of halogen which is transferred from the titanium oxide to a liquid phase is at least 90 mass% on the basis of the entire amount of halogen contained in the titanium oxide.

(3) A titanium oxide according to (1) or (2) above, which comprises Fe in an amount of 100 mass ppm or less, Al in an amount of 100 mass ppm or less, Si in an amount of 100 mass ppm or less, and S in an amount of 100 mass ppm or less.

(4) A titanium oxide according to any one of (1) through (3) above, which has a specific surface area of 10 to 200 m^2/g.

(5) A titanium oxide according to any one of (1) through (4) above, which comprises anatase as a primary phase.

(6) A titanium oxide according to (5) above, which has an anatase content of at least 90%.

(7) A titanium oxide according to any one of (1) through (4) above, which comprises brookite as a primary phase.

(8) A titanium oxide according to (7) above, which has a brookite content of at least 90%.

(9) A titanium oxide according to any one of (1) through (8) above, which has a 90% cumulative mass particle size of 2.5 μm or less as measured by use of a laser diffraction particle size analyzer.

(10) A titanium oxide according to any one of (1) through (9) above, wherein said titanium halogenide is titanium tetrachloride and said halogen is chlorine.

(11) A vapor-phase process for producing a titanium oxide, comprising reacting a titanium halogenide-containing gas with an oxidative gas, characterized in that, when the titanium halogenide-containing gas and the oxidative gas are introduced into a reactor, to thereby allow reaction to proceed, the temperature of the interior of the reactor is at least 800°C but less than 1,100°C.

(12) A process for producing a titanium oxide according to (11) above, wherein the residence time of the titanium halogenide-containing gas and the oxidative gas in the reactor at temperature range of at least 800°C but less than 1,100°C is 0.1 seconds or less.

(13) A process for producing a titanium oxide according to (11) or (12) above, wherein each of the titanium halogenide-containing gas and the oxidative gas is preliminarily heated at a temperature of at least 600°C but less than 1,100°C before being introduced into the reactor.

(14) A process for producing a titanium oxide according to any one of (11) through (13) above, wherein reaction is performed by use of a raw material gas mixture containing titanium halogenide and an inert gas at a ratio of 1 : 0.1 - 20 by mol, and also by use of an oxidative gas whose amount is 1 to 30 mol on the basis of 1 mol of the titanium halogenide.

(15) A process for producing a titanium oxide according to any one of (11) through (14) above, wherein the oxidative gas is an oxygen gas containing water steam.

(16) A process for producing a titanium oxide according to (15) above, wherein the oxidative gas contains steam in an amount of at least 0.1 mol per 1 mol of an oxygen gas.

(17) A process for producing a titanium oxide according to any one of (11) through (16) above, wherein said titanium halogenide is titanium tetrachloride.

(18) A process for producing a titanium oxide characterized by comprising dehalogenating titanium oxide produced by the process as set forth in any one of (11) through (17) above by means of a dry dehalogenation method.

(19) A process for producing a titanium oxide according to (18) above, wherein, in the dry dehalogenation method, titanium oxide is heated to 200 to 500°C.

(20) A process for producing a titanium oxide according to (18) above, wherein, in the dry dehalogenation method, a steam-containing gas is heated to 200 to 1,000°C, and is brought into contact with titanium oxide.

(21) A process for producing a titanium oxide according to (20) above, wherein the steam-containing gas is air containing steam in an amount of at least 0.1 vol.%.

(22) A process for producing a titanium oxide according to (20) above, wherein the ratio by mass of the steam to the titanium oxide is at least 0.01.

(23) A process for producing a titanium oxide characterized by comprising dehalogenating titanium oxide produced by the method as set forth in any one of (11) through (17) above by means of a wet dechlorination method, to thereby yield a slurry containing a titanium oxide.

(24) A process for producing a titanium oxide according to (23) above, wherein, in the wet dehalogenation method, titanium oxide is suspended in water, and halogen which

is transferred to a liquid phase is discharged to the outside of the resultant suspension.

(25) A process for producing a titanium oxide according to (23) or (24) above, wherein, in the wet dehalogenation method, separation of chlorine is performed by use of an ultrafiltration membrane.

(26) A process for producing a titanium oxide according to (23) or (24) above, wherein, in the wet dehalogenation method, separation of chlorine is performed by use of a reverse osmosis membrane.

(27) A process for producing a titanium oxide according to (23) or (24) above, wherein, in the wet dechlorination method, separation of chloride is performed by use of a filter press.

(28) A powder characterized by comprising a titanium oxide produced by a method as recited in any one of (11) to (27) above.

(29) A slurry characterized by comprising a titanium oxide produced by a method as recited in any one of (11) through (27) above.

(30) A composition characterized by comprising a titanium oxide produced by a method as recited in any one of (11) through (27) above.

(31) A photocatalytic material characterized by comprising a titanium oxide produced by a method as recited in any one of (11) through (27) above.

(32) A material for a wet solar cell characterized by comprising a titanium oxide produced by a method as recited in any one of (11) through (27) above.

(33) A dielectric raw material characterized by comprising a titanium oxide produced by a method as recited in any one of (11) through (27) above.

(34) A silicone rubber additive characterized by comprising a titanium oxide produced by a method as recited in any one of (11) through (27) above.

(35) A titanium oxide characterized in that the rutile content of the titanium oxide is 5% or less, the specific

surface area as measured by means of a BET one-point
method of the titanium oxide is 10 to 200 m^2/g, the 90%
cumulative mass particle size measured by a laser
diffraction particle size analyzer of the titanium oxide
is 2.5 μm or less, and the specific surface area of the
titanium oxide as measured by means of a BET one-point
method; i.e., B (m^2/g), and the halogen content of the
titanium oxide; i.e., C_i (mass ppm), satisfy the
following relation; $0 \leq C_i \leq 650ke^{0.02B}$ wherein k is 0.20.

(36) A titanium oxide according to (35) above, wherein
the relation $10 < C_i \leq 650ke^{0.02B}$ wherein k is 0.15, is
satisfied.

BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 shows the relation between halogen content
and BET specific surface area of ultrafine particulate
titanium oxide.

MODES FOR CARRYING OUT THE INVENTION

The titanium halogenide as the starting material for
the titanium oxide of the present invention is preferably
titanium chloride, particularly titanium tetrachloride
since they are commercially easily available.
Accordingly, in the following, the present invention is
described with reference to a typical example wherein the
halogen is chlorine, but the present invention may be
applied to the cases wherein the halogen is bromine or
iodine.

The ultrafine particulate titanium oxide of low
rutile content of the present invention contains almost
no chlorine in the interior of each particle, although it
is produced using titanium tetrachloride in a gas-phase
method. Chlorine remaining in the interior of titanium
oxide particles may diffuse toward the surfaces thereof
with passage of time, to thereby corrode or denature a
substrate. Since difficulty is encountered in removing
chlorine remaining in the interior of titanium oxide
particles by means of a simple dechlorination treatment

such as washing with water or drying. Therefore it is
preferred that, chlorine is not present inside the
interior of the particles.

The proportion of chlorine contained in the interior
of titanium oxide particles based on the total amount of
chlorine present on the surface of and in the particles
is determined on the basis of the ratio of the amount of
chlorine extracted from the particles with pure water
(hereinafter simply referred to as "water-extracted
chlorine") to the entire amount of chlorine contained in
the particles. Specifically, the chlorine amount is
calculated by the following formula (1):

$$R = WCL/TCL \times 100 \cdot \cdot \cdot \cdot \cdot \cdot (1)$$

(wherein R represents the percent of chlorine present on
the surfaces of titanium oxide particles (%), WCL
represents the amount of water-extracted chlorine
contained in the particles (mass%), and TCL represents
the entire amount of chlorine contained in the particles
(mass%)). The greater the R value, the smaller the
amount of chlorine contained in the interior of the
titanium oxide particles. In the titanium oxide of the
present invention, R is preferably at least 80%, more
preferably at least 90%.

A characteristic feature of the ultrafine
particulate titanium oxide of the present invention,
which is produced from titanium tetrachloride through a
vapor-phase process, resides in that the titanium oxide
may have a rutile content of 5% or less (hereinafter may
be simply referred to as "low-rutile ultrafine
particulate titanium oxide"), and in that the titanium
oxide may satisfy the relation represented by the
following formula (2):

$$C \leq 650 \times e^{0.02B} \cdot \cdot \cdot \cdot \cdot \cdot (2)$$

, not only after a dechlorination step but also in some
cases even before a dechlorination step. The rutile
content is calculated from the peak height corresponding

to rutile crystals as measured through X-ray
diffractometry; i.e., Hr, the peak height corresponding
to anatase crystals as measured through X-ray
diffractometry; i.e., Ha, and the peak height
corresponding to Brookite crystals as measured through x-
ray diffractometry; i.e., Hb; specifically, the rutile
content is calculated by use of the following formula:
rutile content = 100 × Hr/(Hr + Ha + Hb). In formula
(2), C represents the entire amount of chlorine (mass%)
in the titanium oxide. For example, C is calculated
through the following procedure: a hydrofluoric acid
aqueous solution is added to titanium oxide, and the
titanium oxide is dissolved in the solution under
microwave heating; the resultant solution is subjected to
measurement by means of a potentiometric titration method
employing silver nitrate, to thereby obtain the mass of
chlorine contained in the titanium oxide; and the thus-
obtained chlorine mass is divided by the mass of the
employed titanium oxide. In formula (2), B represents a
BET specific surface area (m^2/g) falling within a range
of 10 to 200 m^2/g).

    The low-rutile ultrafine particulate titanium oxide
of the present invention satisfies the relation of the
aforementioned formula (2) shown in Fig. 1, having a low
total chlorine content, and has a high R as represented
by the aforementioned formula (1), having a low chlorine
content inside the particles. Conventional ultrafine
particulate titanium oxide produced from titanium
tetrachloride through a vapor-phase process has a low
rutile content. However, in the case of such
conventional titanium oxide, the chlorine contents
corresponding to the BET specific surface areas are
plotted in the region above the curve of Fig. 1
represented by the formula: $C = 650 \times e^{0.02B}$, and the
chlorine content inside the particles is high.
Particularly, as the surface area of titanium oxide

increase, dechlorination is more difficult and the
content of chlorine tends to increase exponentially.

The low-rutile ultrafine particulate titanium oxide
of the present invention satisfies the relation between
5   the chlorine content and the BET specific surface area
represented by formula (2), and has a BET specific
surface area of normally 10 to 200 m^2/g, preferably 40 to
200 m^2/g, more preferably 45 to 120 m^2/g.

The low-rutile ultrafine particulate titanium oxide
10   of the present invention has a content of each of Fe, Al,
Si and S of preferably 100 mass ppm or less, more
preferably 0.1 to 100 mass ppm, more preferably 0.1 to 50
mass ppm, are particularly 0.1 to 10 mass ppm.

The contents of less than 0.1 ppm of these
15   impurities can be attained by using high purity starting
materials and highly corrosion resistant reactor and
other equipment. It is economically advantageous that
the contents of each impurity be made less than 0.1 mass
ppm in normal applications of titanium oxide of the
20   present invention.

A characteristic feature of the low-rutile titanium
oxide of the present invention resides in its high
dispersibility. In the present invention, dispersibility
is determined on the basis of particle size distribution
25   as obtained through laser diffraction particle size
distribution analysis. According to "Ultrafine Particle
Handbook" (edited by Shinroku Saito, Fujitec Corporation,
p. 93, (1990)), dispersibility can be determined through,
for example, the precipitation method, microscopy, light
30   scattering, or the direct count method. Of these, the
precipitation method and the direct count method are not
suitable for determination of dispersibility of ultrafine
particles, since the particle size which can be measured
through each of the methods is limited to some hundreds
35   of nm or more. Microscopy is also not preferred, in
consideration that measurements may vary depending on the
sampling process of a sample to be measured or the

preliminary treatment of the sample. In contrast, the
light scattering method is suitable for measurement of
ultrafine particles, since it can measure a particle size
falling within a range of some nm to some μm. A
procedure for measuring particle size distribution will
next be described.

Pure water (50 ml) and a 10% sodium
hexametaphosphate aqueous solution (100 μl) are added to
titanium oxide (0.05 g) to thereby prepare a slurry, and
the slurry is irradiated with ultrasonic waves (46 KHz,
65 W) for three minutes. The resultant slurry is
subjected to measurement by a laser diffraction particle
size distribution analyzer (model: SALD-2000J, product of
Shimadzu Corporation), to thereby measure the particle
size distribution of the titanium oxide. When the 90%
cumulative mass particle size (hereinafter may be simply
referred to as "D90") of the thus-measured particle size
distribution is small, the titanium oxide is considered
to exhibit excellent dispersibility to a hydrophilic
solvent. The 50% cumulative mass particle size may be
employed for determination of dispersibility. However,
in this case, aggregated particles exhibiting low
dispersibility are difficult to detect. The ultrafine
particulate titanium oxide of the present invention
preferably has a D90 of 2.5 μm or less.

The ultrafine particulate titanium oxide of the
present invention may be incorporated into various
compositions as a raw material, a pigment, or a
particulate component exerting a photocatalytic effect.
For example, the titanium oxide may be employed as a raw
material or an additive in a variety of products,
including cosmetic compositions, ultraviolet shielding
materials, dielectric materials, silicone rubber, and
solar cells.

The production process for the titanium oxide will
next be described.

In a generally known vapor-phase process for producing titanium oxide, titanium tetrachloride is oxidized by use of an oxidative gas such as oxygen or steam at about 1,000°C, to thereby yield fine particulate titanium oxide.

In order to produce ultrafine particulate titanium oxide through a vapor-phase process, the growth time (growth zone) of particles must be shortened. Specifically, when cooling or dilution is performed immediately after reaction to thereby shorten the high-temperature residence time of titanium oxide particles, growth of the particles attributed to, for example, sintering can be prevented. When the high-temperature residence time of titanium oxide particles is shortened, thermal transformation from anatase to rutile can be prevented, thereby yielding particles of high anatase content.

In general, titanium oxide produced from titanium tetrachloride through a vapor-phase process contains chlorine in an amount of 0.1 to 2 mass%. The surfaces of anatase-type titanium oxide particles have points to which an element such as chlorine can be bound (density: 13 points/nm^2) (the aforementioned "Titanium Oxide" authored by Manabu Seino). When all the points are bound to chlorine, the amount of chlorine remaining on the surfaces of the titanium oxide particles is theoretically obtained by the following formula (3):

$$Y = 0.077 \times A \cdot \cdot \cdot \cdot (3)$$

(wherein Y represents the amount of chlorine remaining on the surfaces of titanium oxide particles (mass%), and A represents the specific surface area of the particles (m^2/g)). For example, when titanium oxide particles have a specific surface area of 100 m^2/g, the amount of chlorine remaining on the surfaces of the particles is calculated as about 8 mass% according to formula (3).

In a practical reaction process, chlorine is substituted by an oxidative gas, and the amount of

chlorine is equilibrated, because of the difference in
chlorine content between the surfaces of titanium oxide
particles and a vapor phase, so that the chlorine content
of the titanium oxide particles may become somewhat lower
than the value calculated by the aforementioned formula
(3). However, when the high-temperature residence time
of titanium oxide is shortened in the reaction process,
oxidation of titanium tetrachloride is not completed,
thereby possibly increasing the amount of partially
chlorinated titanium oxide. When chlorine remains in the
interior of titanium oxide particles; i.e., when the
amount of chlorine contain in the interior of the
particles increases, high-temperature or long-term
heating treatment is required for removing chlorine from
the particles, and as a result, the specific surface area
of the particles is reduced. Conventional ultrafine
particulate titanium oxide produced through a vapor-phase
process has high anatase content but high chlorine
content, or has low chlorine content but low anatase
content.

The present inventors have found that, in a vapor-
phase process for producing titanium oxide through
reaction (high-temperature oxidation) between a titanium-
tetrachloride-containing gas and an oxidative gas, when a
titanium tetrachloride-containing gas which has been
heated to a temperature of at least 600°C but less than
1,100°C and an oxidative gas which has been heated to a
temperature of at least 600°C but less than 1,100°C are
fed to a reaction tube, to thereby allow reaction to
proceed, and the resultant titanium oxide is held within
the reaction tube for 0.1 seconds or less at a
temperature of at least 800°C but less than 1,100°C and
then subjected to dechlorination, low-entire chlorine and
particularly low-particle interior chlorine, low-rutile
ultrafine particulate titanium oxide having high BET
specific surface area can be produced; and when the above
produced titanium oxide is further subjected to a

dechlorination step, lower-entire chlorine and low particle interior chlorine, low-rutile ultrafine particulate titanium oxide can be obtained.

Dechlorination of titanium oxide is performed by means of a dry method or a wet method. In a dry dechlorination method, for example, titanium oxide is heated by use of a heating apparatus, to thereby remove chlorine from the titanium oxide. Examples of the heating apparatus employed in the dry dechlorination method include, but are not limited to, a cylindrical rotatable heating furnace, a hot-air circulation heating furnace, a flow drying furnace, and a stirring drying furnace. In a wet dechlorination method, for example, titanium oxide is suspended in pure water, and chlorine which is transferred to a liquid phase is discharged to the outside of the resultant suspension. After chlorine is discharged to the outside of the suspension, the resultant titanium oxide may be dried.

The temperature of the interior of a reaction tube to which a titanium tetrachloride-containing gas and an oxidative gas are fed is preferably at least 800°C but less than 1,100°C, more preferably at least 900°C but less than 1,000°C. When the temperature of the interior of the reaction tube is increased, reaction between these gases is completed simultaneous with mixing of these gases, thereby promoting uniform nucleus generation and reducing the zone of reaction (CVD). When the temperature of the interior of the reaction tube is lower than 800°C, titanium oxide of high anatase content is readily produced, but reaction proceeds incompletely, and thus chlorine remains in the interior of the resultant titanium oxide particles. In contrast, when the temperature of the interior of the reaction tube is 1,100°C or higher, anatase-to-rutile transformation or growth of particles proceeds, and thus low-rutile ultrafine particulate titanium oxide fails to be produced.

When a raw material gas is fed to a reaction tube,
reaction (exothermic reaction) proceeds, and a reaction
zone having a temperature higher than 1,100°C is formed
within the tube. Although a certain amount of heat is
released from the reaction tube, if rapid cooling of the
tube is not performed, titanium oxide particles continue
to grow, and the crystal form of the particles is
transformed to rutile. Therefore, in the present
invention, the high-temperature resistance time of
titanium oxide particles at a temperature of at least
800°C but less than 1,100°C is preferably regulated to
0.1 seconds or less, more preferably 0.005 to 0.1
seconds, particularly 0.01 to 0.05 seconds. When the
high-temperature residence time exceeds 0.1 seconds,
anatase-to-rutile transformation or sintering of the
particles proceeds. When the high-temperature residence
time is less than 0.005 seconds, the oxidation reaction
time of titanium tetrachloride becomes short and the
reaction should be conducted under the conditions in
which oxidation is accelerated, for example, using an
excess amount of oxygen in comparison with titanium
tetrachloride. If oxidation is not sufficient, the
residual chlorine inside the particles may increase.

Rapid cooling of the reaction tube is performed by
means of, for example, a method in which a large amount
of gas, such as cooling air or nitrogen, is introduced
into the reaction mixture, or a method in which water is
sprayed to the reaction tube.

When the temperature of the interior of the reaction
tube is regulated to at least 800°C but less than
1,100°C, ultrafine particulate titanium oxide having low
chlorine content can be produced. When the high-
temperature residence time is regulated to 0.1 seconds or
less, anatase-to-rutile transformation and growth of
particles can be prevented.

In order to regulate the temperature of the interior
of the reaction tube to at least 800°C but less than

1,100°C, the heating temperature of the raw material gas
is preferably regulated to 600°C to 1,100°C inclusive.
The thus-heated raw material gas undergoes reaction in
the reaction tube, to thereby generate heat. However,
when the temperature of the raw material gas is lower
than 600°C, the temperature of the interior of the
reaction tube tends not to become 800°C or higher. In
contrast, when the temperature of the raw material gas is
1,100°C or higher, although a certain amount of heat is
released from the reaction tube, the temperature of the
interior of the tube tends to exceed 1,100°C.

In the raw material gas containing titanium
tetrachloride, the amount of an inert gas is preferably
0.1 to 20 mol, more preferably 4 to 20 mol, on the basis
of 1 mol of titanium tetrachloride gas. When the amount
of the inert gas falls below the above range, the density
of titanium oxide particles in the reaction zone
increases, and aggregation or sintering of the particles
tends to occur, whereby ultrafine particulate titanium
oxide may fail to be produced. In contrast, when the
amount of the inert gas exceeds the above range,
reactivity is lowered, and the yield of titanium oxide is
reduced.

The oxidative gas should contain oxygen. The amount
of an oxygen gas to be reacted with the titanium
tetrachloride-containing raw material gas is preferably 1
to 30 mol, more preferably 5 to 30 mol, on the basis of 1
mol of titanium tetrachloride. When the amount of the
oxygen gas is increased, large amounts of nuclei are
generated, and ultrafine particulate titanium oxide is
readily produced. However, even when the amount of the
oxygen gas is increased so as to exceed 30 mol, the
amount of nuclei to be generated no longer increases.
Therefore, from the viewpoint of economy, an upper limit
is imposed on the amount of the oxygen, although
properties of the resultant titanium oxide do not vary
even when the amount of the oxygen gas exceeds 30 mol.

When the amount of the oxygen gas is insufficient with
respect to that of titanium tetrachloride, oxygen defects
in the resultant titanium oxide increase in number, and
the titanium oxide is colored. The oxidative gas may
contain steam in addition to oxygen.

The oxidative gas may be any of, for example,
oxygen, steam-containing oxygen, air, a mixed gas thereof
with an inert gas such as nitrogen or argon, but is
preferably oxygen containing steam (water steam) since
the reaction temperature can be easily controlled.

Dechlorination of titanium oxide through heating is
preferably performed at a heating temperature of 200°C to
500°C while titanium oxide powder is brought into contact
with steam, such that the ratio by mass of water to
titanium oxide (i.e., the mass of steam/the mass of
titanium oxide, the same shall apply hereinafter) is 0.01
or more. More preferably, dechlorination of titanium
oxide is performed under the following conditions: mass
ratio of water to titanium oxide: 0.04 or more, heating
temperature: 250°C to 450°C. When the heating
temperature exceeds 500°C, sintering of titanium oxide
particles proceeds, and growth of the particles occurs,
whereas when the heating temperature is lower than 200°C,
efficiency in dechlorination is considerably lowered.
Dechlorination proceeds through substitution of chlorine
on the surfaces of titanium oxide particles by water
present in the vicinity of the particles or by hydroxyl
groups present on the surfaces of adjacent particles. In
the case where chlorine on the surfaces of titanium oxide
particles is substituted by water, dechlorination
proceeds without growth of the particles. Meanwhile, in
the case where chlorine on the surfaces of titanium oxide
particles is substituted by hydroxyl groups present on
the surfaces of adjacent particles, dechlorination
proceeds simultaneously with growth of the particles.
Particularly, titanium oxide having a larger surface area
may more easily grain grow since the possibility of

substitution reaction with hydroxide on the surface of
adjacent particles increases. Therefore, when
dechlorination is performed while growth of particles is
suppressed, regulation of the mass ratio of water to
titanium oxide becomes critical. When the mass ratio of
water to titanium oxide is preferably 0.01 or more,
growth of particles can be suppressed.

Preferably, steam with which titanium oxide is
brought into contact is mixed with a gas capable of
discharging chlorine removed from the titanium oxide to
the outside at high efficiency. Examples of such a gas
include air. When air is employed, the amount of steam
contained therein is preferably at least 0.1 vol.%, more
preferably at least 5 vol.%, much more preferably at
least 10 vol.%. Air containing steam is preferably
heated to 200°C to 1,000°C.

Since the low-rutile ultrafine particulate titanium
oxide of the present invention contains almost no
chlorine in the interior of each particle, the chlorine
content of the titanium oxide may be reduced by means of
a wet method. In a wet dechlorination method, for
example, the titanium oxide is suspended in water, and
chlorine which transfers to a liquid phase is discharged
to the outside of the resultant suspension by use of an
ultrafiltration membrane, a reverse osmosis membrane, or
a filter press.

The low-rutile, low-entire halogen, particularly
low-particle interior halogen, ultrafine titanium oxide
of the present invention can provide low-rutile ultrafine
titanium oxide having a very low entire halogen content
in relation to the BET specific surface area, preferably
by removing halogen on the surface of particle more
completely.

The low-rutile, low-entire halogen and low-interior
halogen, ultrafine titanium oxide of the present
invention is characterized in that the rutile content of
the titanium oxide is 5% or less, the specific surface

area as measured by means of a BET one-point method of
the titanium oxide is 10 to 200 m^2/g, the 90% cumulative
mass particle size measured by a laser diffraction
particle size analyzer of the titanium oxide is 2.5 μm or
less, and the specific surface area of the titanium oxide
as measured by means of a BET one-point method; i.e., B
(m^2/g), and the halogen content in the interior of the
titanium oxide particles; i.e., C_i (mass ppm), satisfy
the following relation: $0 < C_i \leq 650ke^{0.02B}$ wherein k is
0.20, more preferably $0 < C_i \leq 650ke^{0.02B}$ wherein k is
0.20, further preferably $10 < C_i \leq 650ke^{0.02B}$ wherein k is
0.15.

EXAMPLES
The present invention will next be described in
detail by way of Examples, which should not be construed
as limiting the invention thereto.

Example 1:
A diluted titanium tetrachloride gas which had been
prepared by diluting gaseous titanium tetrachloride (11.8
Nm^3/hr, wherein N refers to "normal state," the same
shall apply hereinafter) with nitrogen gas (8 Nm^3/hr) was
preliminarily heated to 900°C. Separately, an oxidative
gas which had been prepared by mixing oxygen (8 Nm^3/hr)
with steam (32 Nm^3/hr) was preliminarily heated to 800°C.
These raw material gases were introduced into a quartz-
glass-made reaction tube. Cooling air was introduced
into the reaction tube such that the residence time of
the raw material gasses at a temperature of at least
800°C but less than 1,100°C was 0.1 seconds, and
subsequently the resultant ultrafine particulate titanium
oxide powder was collected by use of a
polytetrafluoroethylene-made bag filter.
The thus-obtained titanium oxide powder was cause to
flow through a cylindrical rotatable heating furnace, and
subjected to dechlorination under the following
conditions: mass ratio of water to titanium oxide: 0.02,

heating temperature: 450°C. The thus-dechlorinated titanium oxide powder was found to have a BET specific surface area of 22 m²/g, a rutile content of 1%, a water-extracted chlorine content of 900 mass ppm, and a total chlorine content of 1,000 mass ppm. The BET specific surface area was measured by use of a specific surface area measuring apparatus (model: Flow Sorb II, 2300, product of Shimadzu Corporation). The rutile content was calculated from the peak height corresponding to rutile crystals as measured through X-ray diffractometry; i.e., Hr, the peak height corresponding to anatase crystals as measured through X-ray diffractometry; i.e., Ha and the peak height corresponding to brookite crystals as measured through x-ray diffractometry; i.e., Hb. Specifically, the rutile content was calculated by use of the following formula: rutile content = 100 × Hr/(Hr + Ha + Hb). The amount of chlorine present on the surfaces of the titanium oxide powder (hereinafter simply referred to as "surface chlorine content") was calculated from the above-obtained water-extracted chlorine content (900 mass ppm) and total chlorine content (1,000 mass ppm) by use of the aforementioned formula (1), and was found to be greater than 80%. Total chlorine content was found to be lower than the value calculated from the above-obtained specific surface area (22 m²/g) by use of the aforementioned formula (2).

The 90% cumulative mass particle size (D90) of the above-obtained titanium oxide powder was measured by means of laser diffraction particle size distribution analysis, and was found to be 1.1 μm. Table 1 shows the analysis results, including rutile content, BET specific surface area, total chlorine content, surface chlorine content, D90, Fe content, Al content, Si content, and S content.

Example 2:

A diluted titanium tetrachloride gas which had been

prepared by diluting gaseous titanium tetrachloride (5.9 Nm^3/hr) with nitrogen gas (30 Nm^3/hr) was preliminarily heated to 1,000°C. Separately, an oxidative gas which had been prepared by mixing oxygen (4 Nm^3/hr) with steam
5   (16 Nm^3/hr) was preliminarily heated to 1,000°C. These raw material gases were introduced into a quartz-glass-made reaction tube. Cooling air was introduced into the reaction tube such that the residence time of the raw material gasses at a temperature of at least 800°C but
10   less than 1,100°C was 0.03 seconds, and subsequently the resultant ultrafine particulate titanium oxide powder was collected by use of a polytetrafluoroethylene-made bag filter.

     The thus-obtained titanium oxide powder was fed to a
15   hot-air circulation heating furnace, and subjected to dechlorination under the following conditions: mass ratio of water to titanium oxide: 0.04, heating temperature: 450°C. The thus-dechlorinated titanium oxide powder was found to have a BET specific surface area of 65 m^2/g, a
20   rutile content of 3%, a water-extracted chlorine content of 900 mass ppm, and a total chlorine content of 1,100 mass ppm. The surface chlorine content was calculated from the above-obtained water-extracted chlorine content (900 mass ppm) and total chlorine content (1,100 mass
25   ppm) by use of the aforementioned formula (1), and was found to be greater than 80%. The total chlorine content was found to be lower than the value calculated from the above-obtained specific surface area (65 m^2/g) by use of the aforementioned formula (2). The 90% cumulative mass
30   particle size (D90) of the above-obtained titanium oxide powder was measured by means of laser diffraction particle size distribution analysis, and was found to be 1.9 μm. Table 1 shows the analysis results, including rutile content, BET specific surface area, total chlorine
35   content, surface chlorine content, D90, Fe content, Al content, Si content, and S content.
     Example 3:

A diluted titanium tetrachloride gas which had been prepared by diluting gaseous titanium tetrachloride (4.7 Nm^3/hr) with nitrogen gas (36 Nm^3/hr) was preliminarily heated to 1,000°C. Separately, an oxidative gas which

5 had been prepared by mixing air (36 Nm^3/hr) with steam (25 Nm^3/hr) was preliminarily heated to 1,000°C. These raw material gases were introduced into a quartz-glass-made reaction tube. Cooling air was introduced into the reaction tube such that the residence time of the raw

10 material gasses at a temperature of at least 800°C but less than 1,100°C was 0.02 seconds, and subsequently the resultant ultrafine particulate titanium oxide powder was collected by use of a polytetrafluoroethylene-made bag filter.

15 The thus-obtained titanium oxide powder was fed to a hot-air circulation heating furnace, and subjected to dechlorination under the following conditions: mass ratio of water to titanium oxide: 0.06, heating temperature: 350°C. The thus-dechlorinated titanium oxide powder was

20 found to have a BET specific surface area of 97 m^2/g, a rutile content of 1%, a water-extracted chlorine content of 1,800 mass ppm, and a total chlorine content of 2,000 mass ppm. The surface chlorine content was calculated from the above-obtained water-extracted chlorine content

25 (1,800 mass ppm) and total chlorine content (2,000 mass ppm) by use of the aforementioned formula (1), and was found to be greater than 80%. The total chlorine content was found to be lower than the value calculated from the above-obtained specific surface area (97 m^2/g) by use of

30 the aforementioned formula (2). The 90% cumulative mass particle size (D90) of the above-obtained titanium oxide powder was measured by means of laser diffraction particle size distribution analysis, and was found to be 2.2 μm. Table 1 shows the analysis results, including

35 rutile content, BET specific surface area, total chlorine content, surface chlorine content, D90, Fe content, Al content, Si content, and S content.

Comparative Example 1:

    A diluted titanium tetrachloride gas which had been prepared by diluting gaseous titanium tetrachloride (11.8 Nm^3/hr) with nitrogen gas (8 Nm^3/hr) was preliminarily heated to 900°C. Separately, an oxidative gas which had been prepared by mixing oxygen (8 Nm^3/hr) with steam (32 Nm^3/hr) was preliminarily heated to 800°C. These raw material gases were introduced into a quartz-glass-made reaction tube. Cooling air was introduced into the reaction tube such that the residence time of the raw material gasses at a temperature of at least 800°C but less than 1,100°C was 0.2 seconds, and subsequently the resultant ultrafine particulate titanium oxide powder was collected by use of a polytetrafluoroethylene-made bag filter.

    The thus-obtained titanium oxide powder was caused to flow through a cylindrical rotatable heating furnace, and subjected to dechlorination under the following conditions: mass ratio of water to titanium oxide: 0.02, heating temperature: 450°C. The thus-dechlorinated titanium oxide powder was found to have a BET specific surface area of 19 m^2/g, a rutile content of 11%, a water-extracted chlorine content of 300 mass ppm, and a total chlorine content of 300 mass ppm. The surface chlorine content was calculated from the above-obtained water-extracted chlorine content (300 mass ppm) and total chlorine content (300 mass ppm) by use of the aforementioned formula (1), and was found to be greater than 80%. The total chlorine content was found to be lower than the value calculated from the above-obtained specific surface area (19 m^2/g) by use of the aforementioned formula (2). The 90% cumulative mass particle size (D90) of the above-obtained titanium oxide powder was measured by means of laser diffraction particle size distribution analysis, and was found to be 0.8 μm. Table 1 shows the analysis results, including rutile content, BET specific surface area, total chlorine

content, surface chlorine content, D90, Fe content, Al
content, Si content, and S content.
Comparative Example 2:

A diluted titanium tetrachloride gas which had been
prepared by diluting gaseous titanium tetrachloride (4.7
Nm^3/hr) with nitrogen gas (36 Nm^3/hr) was preliminarily
heated to 800°C. Separately, an oxidative gas which had
been prepared by mixing air (36 Nm^3/hr) with steam (25
Nm^3/hr) was preliminarily heated to 800°C. These raw
material gases were introduced into a quartz-glass-made
reaction tube. The temperature of the reaction tube was
regulated to 750°C, and cooling air was introduced into
the reaction tube such that the residence time of the raw
material gasses was 0.08 seconds. Thereafter, the
resultant ultrafine particulate titanium oxide powder was
collected by use of a polytetrafluoroethylene-made bag
filter.

The thus-obtained titanium oxide powder was fed to a
hot-air circulation heating furnace, and subjected to
dechlorination under the following conditions: mass ratio
of water to titanium oxide: 0.04, heating temperature:
350°C. The thus-dechlorinated titanium oxide powder was
found to have a BET specific surface area of 74 m^2/g, a
rutile content of 2%, a water-extracted chlorine content
of 2,800 mass ppm, and a total chlorine content of 3,900
mass ppm. The surface chlorine content was calculated
from the above-obtained water-extracted chlorine content
(2,800 mass ppm) and total chlorine content (3,900 mass
ppm) by use of the aforementioned formula (1), and was
found to be lower than 80%. The total chlorine content
was found to be greater than the value calculated from
the above-obtained specific surface area (74 m^2/g) by use
of the aforementioned formula (2). The 90% cumulative
mass particle size (D90) of the above-obtained titanium
oxide powder was measured by means of laser diffraction
particle size distribution analysis, and was found to be
3.6 μm. Table 1 shows the analysis results, including

rutile content, BET specific surface area, total chlorine content, surface chlorine content, D90, Fe content, Al content, Si content, and S content.

Comparative Example 3:

A diluted titanium tetrachloride gas which had been prepared by diluting gaseous titanium tetrachloride (5.9 Nm³/hr) with nitrogen gas (30 Nm³/hr) was preliminarily heated to 1,100°C. Separately, an oxidative gas which had been prepared by mixing oxygen (4 Nm³/hr) with steam (16 Nm³/hr) was preliminarily heated to 1,100°C. These raw material gases were introduced into a quartz-glass-made reaction tube. The temperature of the reaction tube was regulated to 1,200°C, and cooling air was introduced into the reaction tube such that the residence time of the raw material gasses was 0.04 seconds. Thereafter, the resultant ultrafine particulate titanium oxide powder was collected by use of a polytetrafluoroethylene-made bag filter.

The thus-obtained titanium oxide powder was fed to a hot-air circulation heating furnace, and subjected to dechlorination under the following conditions: mass ratio of water to titanium oxide: 0.06, heating temperature: 450°C. The thus-dechlorinated titanium oxide powder was found to have a BET specific surface area of 44 m²/g, a rutile content of 12%, a water-extracted chlorine content of 1,200 mass ppm, and a total chlorine content of 1,300 mass ppm. The surface chlorine content was calculated from the above-obtained water-extracted chlorine content (1,200 mass ppm) and total chlorine content (1,300 mass ppm) by use of the aforementioned formula (1), and was found to be greater than 80%. The total chlorine content was found to be lower than the value calculated from the above-obtained specific surface area (44 m²/g) by use of the aforementioned formula (2). The 90% cumulative mass particle size (D90) of the above-obtained titanium oxide powder was measured by means of laser diffraction particle size distribution analysis, and was found to be

1.2 µm. Table 1 shows the analysis results, including
rutile content, BET specific surface area, total chlorine
content, surface chlorine content, D90, Fe content, Al
content, Si content, and S content.

5   Comparative Example 4:

Commercially available titanyl sulfate (Kanto
Chemical Company, 1st grade chemical) was boiled and the
obtained precipitation was washed with pure water to
obtain water-containing titanium oxide. The water-

10   containing titanyl sulfate was added with pure water to
form a slurry in order to remove the residual sufaic acid
and, while stirring, the slurry was added with an aqueous
ammonia solution to adjust pH to 5 and the stirring was
continued for 12 hours. The slurry was concentrated by a

15   ultrafiltration membrane to a concentration of 20% by
mass. The concentrated slurry was again added with an
aqueous ammonia solution to adjust pH to 5, stirring was
effected for 12 hours, and ultrafiltration was conducted
using a ultrafiltration membrane while adding pure water

20   to obtain a titania sol. The obtained titania sol was
dried at 300°C for 2 hours to obtain a wet-method
ultrafine titanium oxide.

The obtained titanium oxide has a BET specific
surface area of 212 m²/g and, a rutile content of 1%.

25   The water-extracted chlorine content are the total
chlorine content of the titanium oxide were both mass
ppm. The titanium oxide was disassociated with a
crucible and the particle size distribution was measured
by a laser diffraction particle size distribution analyer

30   to have a 90% accumulative mass particle size D90 of 26.1
µm. The rutile content, BET specific surface, total
chlorine content, surface chlorine content, D90, and
analysis results of Fe, Al, Si and S, are shown is Table
1.

Table 1

		Example 1	Example 2	Example 3	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
Rutile content	%	1	3	1	11	2	12	1
BET specific surface area	m²/g	22	65	97	19	74	44	212
Total chlorine content	mass ppm	1,000	1,100	2,000	300	3,900	1,300	<10
Surface chlorine content	%	90	91	90	100	72	92	-
D90	μm	1.1	1.9	2.2	0.8	3.6	1.2	26.1
Fe	mass ppm	<10	<10	<10	<10	<10	<10	50
Al	mass ppm	<10	<10	<10	<10	<10	<10	<10
Si	mass ppm	<20	<20	<20	<20	<20	<20	<20
S	mass ppm	<10	<10	<10	<10	<10	<10	670

INDUSTRIAL APPLICABILITY

The present invention provides anatase-type ultrafine particulate titanium oxide produced through a vapor-phase process, which has low halogen content and exhibits excellent dispersibility as compared with conventional titanium oxide having a BET specific surface area comparable to that of the ultrafine particulate titanium oxide. When the ultrafine particulate titanium oxide is subjected to dehalogenation, the titanium oxide satisfies the relation between BET surface area (B) and halogen content (C) represented by the aforementioned formula (2). The ultrafine particulate titanium oxide has a D90 of 2.5 μm or less as measured by means of laser diffraction particle size analysis. The present invention also provides a process for producing the ultrafine particulate titanium oxide.

The titanium oxide of the present invention is suitable for use in photocatalysts and solar cells. Since the titanium oxide exhibits excellent dispersibility to an aqueous solvent, the titanium oxide can be suitably used for photocatalyst applications in water. The titanium oxide as a powder requires no pulverization process, or requires only a pulverization process employing very simple pulverization equipment. Therefore, the titanium oxide is very advantageously employed in practice in the industry.